

533 Rec'd PCT/PTO 11 AUG 2000

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PATENT

Attorney Docket No. 5725.0632-00



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re National Phase)
Application of PCT/FR98/02831:)
Gérard LANG et al.) Group: Not Yet Assigned
Serial No.: 09/600,128 ✓) Examiner: Not Yet Assigned
PCT Filed: December 22, 1998)
National Stage Entry: July 12, 2000)

For: KERATINOUS FIBRE OXIDATION DYEING COMPOSITION CONTAINING
LACCASE AND DYEING METHOD USING SAME

Assistant Commissioner for Patents
Washington, D.C. 20231

TRANSMITTAL LETTER

Sir:

Enclosed is a Preliminary Amendment for the above identified application.

The claims are calculated below:

	Claims Remaining After Amendment		Highest Number Previously Paid	Present Extra	Rate	Additional Fee
Total	34	-	30	4	x \$ 18	\$72.00
Indep.	4	-	3	1	x \$ 78	\$78.00
[] First Presentation of Multiple Dep. Claim(s)					+\$260	
					Subtotal	\$150.00
Reduction by 1/2 if small entity						-
						TOTAL \$150.00

A check for \$150.00 to cover the cost of the additional claims added by this Preliminary

Amendment is enclosed.

08/15/2000 ERIMANDO 00000046 09600128

01 FC:966
02 FC:964

72.00 DP
78.00 DP

LAW OFFICES
FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N.W.
WASHINGTON, DC 20005
202-408-4000

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

International Application. No.	International Filing Date	Priority Date Claimed
PCT/FR98/02831	December 22, 1998	January 13, 1998

Title of Invention: KERATINOUS FIBRE OXIDATION DYEING COMPOSITION CONTAINING A LACCASE AND DYEING METHOD USING SAME

Applicant(s) For DO/EO/US: Gérard LANG, and Jean COTTERET

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. A copy of the International Application as filed (35 U.S.C. 371(c) (2))
 - a. is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. has been transmitted by the International Bureau.
 - c. is not required, as the application was filed in the United States Receiving Office (RO/US).
6. A translation of the International Application into English (35 U.S.C. 371(c) (2)).
7. Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c) (3)).
 - a. are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. have been transmitted by the International Bureau.
 - c. have not been made; however, the time limit for making such amendments has NOT expired.
 - d. have not been made and will not be made.
8. A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c) (3)).
9. An oath or declaration of the inventor(s) (35 U.S.C. 371(c) (4)).
10. A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c) (5)).

Items 11. to 16. below concern other document(s) or information included:

11. An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. A FIRST preliminary amendment.
14. A SUBSTITUTE specification.
15. A change of power of attorney and/or address letter.
16. Other items or information:
 - a. Verified Small Entity Statement.
 - b. Copy of Notification of Missing Requirements.

09/600128

534 Rec'd PCT/PTR 12 JUL 2008

17. [X] The following fees are submitted:

Basic National Fee (37 CFR 1.492(a)(1)-(5)):

Search Report has been prepared by the EPO or JPO.....\$840.00

International preliminary examination fee paid to

USPTO (37 CFR 1.482).....\$670.00

No international preliminary examination fee paid to

USPTO (37 CFR 1.482) but international search fee

paid to USPTO (37 CFR 1.445(a)(2)).....\$690.00

Neither international preliminary examination fee

(37 CFR 1.482) nor international search fee

(37 CFR 1.445(a)(2)) paid to USPTO.....\$970.00

International preliminary examination fee paid to USPTO

(37 CFR 1.482) and all claims satisfied provisions

of PCT Article 33(1)-(4).....\$ 96.00

ENTER APPROPRIATE BASIC FEE AMOUNT = \$840.00

Surcharge of \$130.00 for furnishing the oath or declaration later than

[] 20 [] 30 months from the earliest claimed priority date

(37 CFR 1.492(e)).

Claims	Number Filed	Number Extra	Rate	
Total Claims	33-20=	13	X \$18.00	\$234.00
Independent Claims	1- 3=		X \$78.00	\$
Multiple dependent claim(s) (if applicable)			+\$260.00	\$260.00
				TOTAL OF ABOVE CALCULATIONS = \$1334.00

Reduction by 1/2 for filing by small entity, if applicable. Verified

Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28)

SUBTOTAL = \$1334.00

Processing fee of \$130.00 for furnishing the English translation later

than [] 20 [] 30 months from the earliest claimed priority date

(37 CFR 1.492(f)).

TOTAL NATIONAL FEE = \$1334.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The

assignment must be accompanied by an appropriate cover sheet

(37 CFR 3.28, 3.31).

\$40.00 per property + \$

TOTAL FEES ENCLOSED = \$1334.00

Amount to be

refunded \$

charged \$

a. [X] A check in the amount of \$ 1334.00 to cover the above fees is enclosed.

b. [] Please charge my Deposit Account No. _____ in the amount of

\$ _____

to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 06-0916. A duplicate copy of this sheet is enclosed.

The Commissioner is hereby authorized to charge any other fees due under 37 C.F.R. §1.16 or §1.17 during the pendency of this application to our Deposit Account No. 06-0916.

SEND ALL CORRESPONDENCE TO:

Finnegan, Henderson, Farabow

Garrett & Dunner, L.L.P.

1300 I Street, N.W.

Washington, D.C. 20005-3315

EFC/FPD/dvz



Ernest F Chapman

Reg. No. 25,961

Submitted: July 12, 2000

PATENT
Attorney Docket No. 5725.0632-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE



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Gérard LANG et al.) Group: Not Yet Assigned
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Examiner: Not Yet Assigned
BOX PCT

For: KERATINOUS FIBRE OXIDATION DYEING COMPOSITION CONTAINING
LACCASE AND DYEING METHOD USING SAME

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

PRELIMINARY AMENDMENT

Prior to the examination of the above-referenced application on the merits,
please amend the application as follows:

IN THE CLAIMS:

Please cancel claims 1-31 without prejudice or disclaimer to the subject matter
contained therein.

Please add new claims 32-65 as follows:

--32. A composition for the oxidation dyeing of keratin fibers, comprising:

- (a) at least one oxidation dye chosen from heterocyclic oxidation bases,
heterocyclic couplers, and acid addition salts of said oxidation dyes; and
- (b) at least one laccase-type enzyme,

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FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N.W.
WASHINGTON, DC 20005
202-408-4000

provided that said heterocyclic oxidation base is not chosen from 4,5-diamino-6-hydroxy-pyrimidine and 3,4-diaminohydroxy-pyrazole, and
provided that said heterocyclic coupler is not chosen from indole, indoline, monocyclic pyridine, and phenazine compounds.

33. The composition according to Claim 32, wherein said keratin fibers are human keratin fibers.

34. The composition according to Claim 33, wherein said human keratin fibers are hair.

35. The composition according to Claim 32, wherein said at least one enzyme of the laccase type is chosen from laccases of plant origin, animal origin, fungal origin and bacterial origin, and laccases obtained by biotechnology.

36. The composition according to claim 32, wherein said at least one enzyme of the laccase type is of plant origin and is chosen from the laccases extracted from plants chosen from Anacardiaceae, Podocarpaceae, Rosmarinus off., Solanum tuberosum, Iris sp., Coffea sp., Daucus carota, Vinca minor, Persea americana, Catharanthus roseus, Musa sp., Malus pumila, Gingko biloba, Monotropa hypopithys, Aesculus sp., Acer pseudoplatanus, Prunus persica, and Pistacia palaestina.

37. The composition according to Claim 32, wherein said at least one enzyme of the laccase type is of microbial origin or obtained by biotechnology.

38. The composition according to Claim 32, wherein said at least one enzyme of the laccase type is chosen from the laccases obtained from fungi chosen from

Polyporus versicolor, Rhizoctonia praticola, Rhus vernicifera, Scytalidium, Polyporus pinsitus, Myceliophthora thermophila, Rhizoctonia solani, Pyricularia orizae, Trametes versicolor, Fomes fomentarius, Chaetomium thermophile, Neurospora crassa, Colorius versicol, Botrytis cinerea, Rigidoporus lignosus, Phellinus noxius, Pleurotus ostreatus, Aspergillus nidulans, Podospora anserina, Agaricus bisporus, Ganoderma lucidum, Glomerella cingulata, Lactarius piperatus, Russula delica, Heterobasidion annosum, Thelephora terrestris, Cladosporium cladosporioides, Cerrena unicolor, Coriolus hirsutus, Ceriporiopsis subvermispora, Coprinus cinereus, Panaeolus papilionaceus, Panaeolus sphinctrinus, Schizophyllum commune, Dichomitus squalens, and variants of all said fungi.

39. The composition according to claim 32, wherein said at least one enzyme of the laccase type is in an amount ranging from 0.5 Lacu to 200 Lacu units per 100 g of said composition.

40. The composition according to claim 32, wherein said heterocyclic oxidation bases are chosen from pyrimidine derivatives, pyrazole derivatives, and acid addition salts of said heterocyclic oxidation bases.

41. The composition according to Claim 40, wherein said pyrimidine derivatives are chosen from 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, pyrazolopyrimidine derivatives, and acid addition salts of said pyrimidine derivatives.

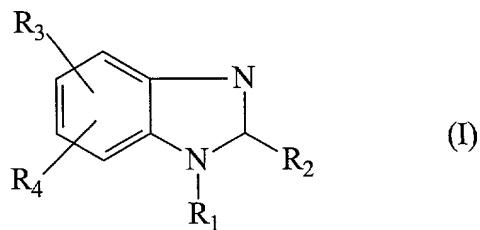
42. The composition according to Claim 41, wherein said pyrazolopyrimidine derivatives are chosen from pyrazolo pyrimidine-3,7-diamine, 2-methylpyrazolo pyrimidine-3,7-diamine, 2,5-dimethyl pyrazolo pyrimidine-3,7-diamine, pyrazolo pyrimidine-3,5-diamine, 2,7-dimethylpyrazolo pyrimidine-3,5-diamine, 3-aminopyrazolo pyrimidin-7-ol, 3-amino-5-methylpyrazolo pyrimidin-7-ol, 3-amino-pyrazolo pyrimidin-5-ol, 2-(3-aminopyrazolo-pyrimidin-7-ylamino)ethanol, 3-amino-7-β-hydroxyethylamino-5-methylpyrazolo pyrimidine, 2-(7-aminopyrazolo pyrimidin-3-ylamino)ethanol, 2-ethanol, 2-ethanol, 5,6-dimethylpyrazolo pyrimidine-3,7-diamine, 2,6-dimethylpyrazolo pyrimidine-3,7-diamine, and 2,5,N7,N7-tetramethylpyrazolo pyrimidine-3,7-diamine, and acid addition salts of said pyrazolopyrimidine derivatives and tautomeric forms of said pyrazolopyrimidine derivatives, when a tautomeric equilibrium exists.

43. The composition according to Claim 40, wherein said pyrazole derivatives are chosen from 4,5-diaminopyrazole, 4,5-diamino-1-methyl-pyrazole, 1-benzyl-4,5-diaminopyrazole, 3,4-diamino-pyrazole, 1-benzyl-4,5-diamino-3-methylpyrazole, 4-amino-1,3-dimethyl-5-hydrazinopyrazole, 4,5-diamino-3-methyl-1-phenylpyrazole, 4,5-diamino-1-tert-butyl-3-methylpyrazole, 4,5-diamino-3-tert-butyl-1-methyl-pyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-1-ethyl-3-(4*i*-methoxyphenyl)pyrazole, 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole, 4,5-diamino-3-hydroxymethyl-1-methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole,

4,5-diamino-3-methyl-1-isopropylpyrazole, and acid addition salts of said pyrazole derivatives.

44. The composition according to claim 32, wherein said heterocyclic couplers are chosen from benzimidazole derivatives, benzomorpholine derivatives, sesamol derivatives, pyrazoloazole derivatives, pyrroloazole derivatives, imidazoloazole derivatives, pyrazolopyrimidine derivatives, pyrazoline-3,5-dione derivatives, pyrrolo-oxazoline derivatives, pyrazolo-thiazole derivatives, thiazoloazole S-oxide derivatives, thiazoloazole S,S-dioxide derivatives, and acid addition salts of said heterocyclic couplers.

45. The composition according to Claim 44, wherein said benzimidazole derivatives are chosen from the compounds of formula (I), and their acid addition salts:



in which:

- R₁ is chosen from hydrogen and C₁-C₄ alkyl groups,
- R₂ is chosen from hydrogen, C₁-C₄ alkyl groups, and phenyl groups,
- R₃ is chosen from hydroxyl groups, amino groups, and methoxy groups,

LAW OFFICES

FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N.W.
WASHINGTON, DC 20005
202-408-4000

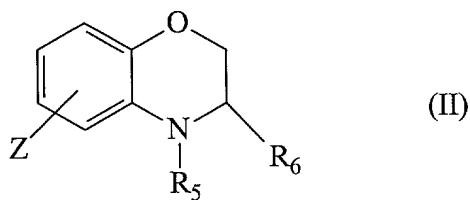
-R₄ is chosen from hydrogen, hydroxyl groups, methoxy groups, and C₁-C₄ alkyl groups;

with the proviso that:

- (a) when R₃ is an amino group, then it occupies position 4;
- (b) when R₃ occupies position 4, then R₄ occupies position 7; and
- (c) when R₃ occupies position 5, then R₄ occupies position 6.

46. The composition according to Claim 44, wherein said benzimidazole derivatives are chosen from 4-hydroxybenzimidazole, 4-amino-benzimidazole, 4-hydroxy-7-methylbenzimidazole, 4-hydroxy-2-methylbenzimidazole, 1-butyl-4-hydroxy-benzimidazole, 4-amino-2-methylbenzimidazole, 5,6-dihydroxybenzimidazole, 5-hydroxy-6-methoxy-benzimidazole, 4,7-dihydroxybenzimidazole, 4,7-dihydroxy-1-methylbenzimidazole, 4,7-dimethoxy-benzimidazole, 5,6-dihydroxy-1-methylbenzimidazole, 5,6-dihydroxy-2-methylbenzimidazole, 5,6-dimethoxy-benzimidazole, and acid addition salts of said benzimidazole derivatives .

47. The composition according to Claim 44, wherein said benzimidazole derivatives are chosen from compounds of formula (II), and their acid addition salts:

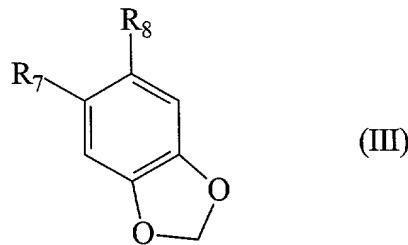


in which:

- R₅ and R₆, which may be identical or different, are each chosen from hydrogen and C₁-C₄ alkyl groups; and
- Z is chosen from hydroxyl groups and amino groups.

48. The composition according to Claim 44, wherein said benzomorpholine derivatives are chosen from 6-hydroxy-1,4-benzomorpholine, N-methyl-6-hydroxy-1,4-benzomorpholine, 6-amino-1,4-benzomorpholine, and acid addition salts of said benzomorpholine derivatives.

49. The composition according to Claim 44, wherein said sesamol derivatives are chosen from the compounds of formula (III) and their acid addition salts:



in which:

- R₇ is chosen from hydroxyl groups, amino groups, (C₁-C₄)alkylamino groups, monohydroxy (C₁-C₄)alkylamino groups, and polyhydroxy(C₂-C₄)alkyl-amino groups;
- R₈ is chosen from hydrogen, halogens, and (C₁-C₄)alkoxy groups.

LAW OFFICES

FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N.W.
WASHINGTON, DC 20005
202-408-4000

50. The composition according to Claim 49, wherein said sesamol derivatives of formula III are chosen from 2-bromo-4,5-methylenedioxyphenol, 2-methoxy-4,5-methylene- dioxyaniline and 2-(β -hydroxy-ethyl)amino-4,5-methylene-dioxybenzene, and acid addition salts of said sesamol derivatives.

51. The composition according to Claim 44, wherein said pyrazoloazole derivatives are chosen from:

- 2-methylpyrazolo-1,2,4-triazole,
- 2-ethylpyrazolo-1,2,4-triazole,
- 2-isopropylpyrazolo-1,2,4-triazole,
- 2-phenylpyrazolo-1,2,4-triazole,
- 2,6-dimethylpyrazolo-1,2,4-triazole,
- 7-chloro-2,6-dimethylpyrazolo-1,2,4-triazole,
- 3,6-dimethylpyrazolo-1,2,4-triazole,
- 6-phenyl-3-methylthiopyrazolo-1,2,4-triazole,
- 6-aminopyrazolo benzimidazole,

and acid addition salts of said pyrazoloazole derivatives.

52. The composition according to Claim 44, wherein said pyrroloazole derivatives are chosen from:

- 5-cyano-4-ethoxycarbonyl-8-methylpyrrolo-1,2,4-triazole,
- 5-cyano-8-methyl-4-phenylpyrrolo-1,2,4-triazole,
- 7-amido-6-ethoxycarbonylpyrrolo benzimidazole,

DOCUMENT EVIDENCE

and acid addition salts of said pyrroloazole derivatives.

53. The composition according to Claim 44, wherein said imidazoloazole derivatives are chosen from:

- 7,8-dicyanoimidazolo imidazole,
- 7,8-dicyano-4-methylimidazolo imidazole,

and acid addition salts of said imidazoloazole derivatives.

54. The composition according to Claim 44, wherein said pyrazolopyrimidine derivatives are chosen from:

- pyrazolo pyrimidin-7-one,
- 2,5-dimethylpyrazolo pyrimidin-7-one,
- 2-methyl-6-ethoxycarbonylpyrazolo pyrimidin-7-one,
- 2-methyl-5-methoxymethylpyrazolo pyrimidin-7-one,
- 2-tert-butyl-5-trifluoromethylpyrazolo pyrimidin-7-one,
- 2,7-dimethylpyrazolo pyrimidin-5-one,

and acid addition salts of said pyrazolopyrimidine derivatives.

55. The composition according to Claim 44, wherein said pyrazoline-3,5-dione derivatives are chosen from:

- 1,2-diphenylpyrazoline-3,5-dione,
- 1,2-diethylpyrazoline-3,5-dione,

and acid addition salts of said pyrazoline-3,5-dione derivatives.

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FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N.W.
WASHINGTON, DC 20005
202-408-4000

56. The composition according to claim 32, wherein said at least one oxidation dye is present in a concentration ranging from about 0.0001% to about 12% by weight relative to the total weight of said composition.

57. The composition according to Claim 32, wherein said at least one oxidation dye is present in a concentration ranging from about 0.005% to about 6% by weight of the total weight of said composition.

58. The composition according to claim 32, further comprising:

(a) at least one benzenic oxidation base chosen from para-phenylenediamines, bis(phenylalkylenediamines, orthophenylenediamines, para-aminophenols, ortho-aminophenols, and acid addition salts of said benzenic oxidation base,

(b) at least one benzenic coupler chosen from meta-phenylenediamines, meta-aminophenols, meta-diphenols and acid addition salts of said benzenic coupler, and

(c) at least one direct dye.

59. The composition according to claim 32, wherein said acid addition salts of said at least one oxidation dye are chosen from hydrochlorides, hydrobromides, sulphates, tartrates, lactates, and acetates.

60. The composition according to claim 32, further comprising at least one carrier which is suitable for dyeing keratin fibers.

61. The composition according to claim 60, wherein said at least one carrier is chosen from water and at least one organic solvent.

62. The composition according to claim 32, wherein said composition has a pH ranging from about 4 to about 11.

63. A method of dyeing keratinous fibers, comprising the step of applying at least one dyeing composition to said keratinous fibers for a sufficient time to achieve a desired coloration, wherein said at least one dyeing composition comprises:

(a) at least one oxidation base chosen from heterocyclic oxidation bases, heterocyclic couplers, and acid addition salts of said oxidation dyes, provided that said heterocyclic oxidation base is not chosen from 4,5-diamino-6-hydroxy- pyrimidine and 3,4-diaminohydroxypyrazole; and provided that said heterocyclic coupler is not chosen from indole, indoline, monocyclic pyridine, and phenazine compounds; and

(b) at least one enzyme of the laccase type.

64. A method for dyeing keratinous fibers comprising the steps of:

(a) storing a first composition;

(b) storing a second composition separately from said first composition;

(c) mixing said first composition with said second composition to form a mixture; and

(d) applying said mixture to said keratinous fibers for a sufficient time to achieve a desired coloration;

wherein said first composition comprises at least one oxidation base chosen from heterocyclic oxidation bases, heterocyclic couplers, and acid addition salts of said oxidation dyes, in a medium appropriate for dyeing keratinous fibers, provided that said

heterocyclic oxidation base is not chosen from 4,5-diamino-6-hydroxy- pyrimidine and 3,4-diaminohydroxypyrazole; and provided that said heterocyclic coupler is not chosen from indole, indoline, monocyclic pyridine, and phenazine compounds; and

wherein said second composition comprises at least one enzyme of the laccase type, in a medium appropriate for dyeing keratinous fibers.

65. A multicompartment device or a dyeing kit, comprising:

a first compartment containing a first composition comprising at least one oxidation base chosen from heterocyclic oxidation bases, heterocyclic couplers, and acid addition salts of said oxidation dyes, provided that said heterocyclic oxidation base is not chosen from 4,5-diamino-6-hydroxy- pyrimidine and 3,4-diaminohydroxypyrazole; and provided that said heterocyclic coupler is not chosen from indole, indoline, monocyclic pyridine, and phenazine compounds, in a medium appropriate for dyeing keratinous fibers; and

a second compartment containing a second composition comprising at least one enzyme of the laccase type, in a medium appropriate for dyeing keratinous fibers.--

REMARKS

Claims 1-31 have been canceled and new claims 32-65 are currently pending in this application. Support for claims 32-65 may be found in the specification as a whole, and claims 1-31, specifically. No new matter has been introduced by the amendments.

LAW OFFICES

FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N.W.
WASHINGTON, DC 20005
202-408-4000

Attorney Docket No.: 5725.0632-00
Serial No. 09/600,128

If there is any fee due in connection with the filing of this Preliminary
Amendment, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

By: *Cheryl Algestrand*
Reg. No 45,275
for Thomas L. Irving
for Reg. No. 28,619

Dated: August 11, 2000.

LAW OFFICES

FINNEGAN, HENDERSON,
FARABOW, GARRETT,
& DUNNER, L.L.P.
1300 I STREET, N.W.
WASHINGTON, DC 20005
202-408-4000

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WO 99/36039

PCT/FR98/02831

1

COMPOSITION FOR THE OXIDATION DYEING OF KERATIN FIBRES,
CONTAINING A LACCASE, AND DYEING PROCESS USING THIS
COMPOSITION

5 The invention relates to a composition for
the oxidation dyeing of keratin fibres, and in
particular of human keratin fibres such as the hair,
comprising, in a medium which is suitable for dyeing,
at least one heterocyclic oxidation dye and at least
10 one laccase-type enzyme, as well as to the dyeing
process using this composition.

It is known practice to dye keratin fibres,
and in particular human hair, with dye compositions
containing one or more oxidation dye precursors, in
15 particular ortho- or para-phenylenediamines, ortho- or
para-aminophenols, and heterocyclic bases, which are
generally known as oxidation bases. These oxidation
dyes (oxidation bases) are colourless or weakly
coloured compounds which, when combined with oxidizing
20 products, can give rise to coloured compounds and dyes
by a process of oxidative condensation.

It is also known that the shades obtained
with these oxidation bases can be varied by combining
them with couplers or coloration modifiers, the latter
25 being chosen in particular from aromatic meta-diamines,
meta-aminophenols, meta-diphenols and certain
heterocyclic compounds.

PCT/FR98/02831

The variety of molecules used as oxidation bases and couplers allows a wide range of colours to be obtained.

The so-called "permanent" coloration obtained 5 by means of these oxidation dyes should moreover satisfy a certain number of requirements. Thus, it should have no toxicological drawbacks, it should allow shades to be obtained in the desired intensity and it should have good staying power with respect to external 10 agents (light, bad weather, washing, permanent-waving, perspiration or rubbing).

The dyes should also allow grey hair to be covered and, finally, they should be as unselective as possible, i.e. they should allow only the smallest 15 possible differences in coloration to be obtained along the same keratin fibre, which may indeed be differently sensitized (i.e. damaged) between its tip and its root.

The oxidation dyeing of keratin fibres is generally carried out in alkaline medium, in the 20 presence of hydrogen peroxide. However, the use of alkaline media in the presence of hydrogen peroxide can have the drawback of resulting in substantial degradation of the fibres, as well as a decolorization of the keratin fibres, which is not always desirable.

25 The oxidation dyeing of keratin fibres can also be carried out using oxidizing systems other than hydrogen peroxide, such as enzymatic systems. Thus, it has already been proposed in US patent 3 251 742 and

patent applications FR-A-2 112 549, FR-A-2 694 018,
EP-A-0 504 005, WO 95/07988, WO 95/33836, WO 95/33837,
WO 96/00290, WO 97/19998 and WO 97/19999, to dye
keratin fibres with compositions comprising at least
5 one oxidation dye, or at least one melanin precursor,
in combination with laccase-type enzymes, the said
compositions being placed in contact with atmospheric
oxygen. Although these dye formulations are used under
conditions which do not result in the degradation of
10 keratin fibres comparable to that generated by dyes
used in the presence of hydrogen peroxide, they lead to
colorations that are still insufficient both in terms
of the homogeneity of the colour distributed along the
fibre (unison) and in terms of the chromaticity
15 (luminosity) and dyeing power.

The Applicant has now discovered that it is
possible to obtain novel dyes that are capable of
giving more intense colorations without generating any
significant degradation of keratin fibres, and that are
20 relatively unselective and stand up well to the various
attacking factors to which the fibres may be subjected,
by combining at least one suitably selected
heterocyclic oxidation dye (oxidation base and/or
coupler) and at least one laccase-type enzyme.

25 This discovery forms the basis of the present
invention.

A first subject of the invention is thus a
ready-to-use composition for the oxidation dyeing of

keratin fibres, and in particular of human keratin fibres such as the hair, characterized in that it comprises, in a medium which is suitable for dyeing,

- at least one oxidation dye chosen from heterocyclic

5 oxidation bases and heterocyclic couplers, and

- at least one laccase-type enzyme,

the said composition being free of heterocyclic coupler chosen from indole, indoline, monocyclic pyridine and phenazine compounds and free of heterocyclic oxidation

10 base chosen from 4,5-diamino-6-hydroxypyrimidine and 3,4-diaminohydroxypyrazole.

The ready-to-use dye composition in accordance with the invention leads to intense, chromatic colorations. The colorations obtained with

15 the ready-to-use dye composition in accordance with the invention moreover show little selectivity and excellent properties of resistance both with respect to atmospheric agents such as light and bad weather and with respect to perspiration and the various treatments

20 to which hair may be subjected (washing, permanent-waving).

A subject of the invention is also a process for the oxidation dyeing of keratin fibres using this ready-to-use dye composition.

25 The laccase(s) used in the ready-to-use dye composition in accordance with the invention can be chosen in particular from laccases of plant origin, of animal origin, of fungal origin (yeasts, moulds or

fungi) or of bacterial origin, it being possible for the organisms of origin to be monocellular or multicellular. The laccase(s) used in the ready-to-use dye composition in accordance with the invention can

5 also be obtained by biotechnology.

Among the laccases of plant origin which can be used according to the invention, mention may be made of the laccases produced by plants which carry out chlorophyll synthesis, such as those mentioned in

10 patent application FR-A-2 694 018.

Mention may be made in particular of the laccases present in extracts of Anacardiaceae plants such as, for example, extracts of *Magnifera indica*, of *Schinus molle* or of *Pleiogynium timoriense*; in extracts

15 of Podocarpacea plants, of *Rosmarinus off.*, of *Solanum tuberosum*, of *Iris sp.*, of *Coffea sp.*, of *Daucus carota*, of *Vinca minor*, of *Persea americana*, of *Catharanthus roseus*, of *Musa sp.*, of *Malus pumila*, of *Gingko biloba*, of *Monotropa hypopithys* (Indian pipe),

20 of *Aesculus sp.*, of *Acer pseudoplatanus*, of *Prunus persica* and of *Pistacia palaestina*.

Among the laccases of fungal origin, optionally obtained by biotechnology, which can be used according to the invention, mention may be made of the

25 laccase(s) obtained from *Polyporus versicolor*, from *Rhizoctonia praticola* and from *Rhus vernicifera* as described, for example, in patent applications FR-A-2 112 549 and EP-A-504 005; the laccases described in

patent applications WO 95/07988, WO 95/33836, WO 95/33837, WO 96/00290, WO 97/19998 and WO 97/19999, the content of which forms an integral part of the present description, such as, for example, the laccase(s) 5 obtained from *Scytalidium*, from *Polyporus pinsitus*, from *Myceliophthora thermophila*, from *Rhizoctonia solani*, from *Pyricularia oryzae*, and variants thereof. Mention may also be made of the laccase(s) obtained from *Trametes versicolor*, from *Fomes fomentarius*, from 10 *Chaetomium thermophile*, from *Neurospora crassa*, from *Colorius versicolor*, from *Botrytis cinerea*, from *Rigidoporus lignosus*, from *Phellinus noxius*, from *Pleurotus ostreatus*, from *Aspergillus nidulans*, from *Podospora anserina*, from *Agaricus bisporus*, from 15 *Ganoderma lucidum*, from *Glomerella cingulata*, from *Lactarius piperatus*, from *Russula delica*, from *Heterobasidion annosum*, from *Thelephora terrestris*, from *Cladosporium cladosporioides*, from *Cerrena unicolor*, from *Coriolus hirsutus*, from *Ceriporiopsis* 20 *subvermispora*, from *Coprinus cinereus*, from *Panaeolus papilionaceus*, from *Panaeolus sphinctrinus*, from *Schizophyllum commune*, from *Dichomitus squalens*, and from variants thereof.

Laccases of fungal origin, optionally 25 obtained by biotechnology, will more preferably be chosen.

The enzymatic activity of the laccases used in accordance with the invention and having

syringaldazine among their substrates can be defined by the oxidation of syringaldazine under aerobic conditions. One Lacu unit corresponds to the amount of enzyme which catalyses the conversion of 1 mmol of

5 syringaldazine per minute at a pH of 5.5 and at a temperature of 30°C. One U unit corresponds to the amount of enzyme which produces an absorbance delta of 0.001 per minute at a wavelength of 530 nm, using syringaldazine as substrate, at 30°C and at a pH of 6.5.

10 The enzymatic activity of the laccases used according to the invention can also be defined by the oxidation of para-phenylenediamine. One ulac unit corresponds to the amount of enzyme which produces an absorbance delta of 0.001 per minute at a wavelength of 496.5 nm, using

15 para-phenylenediamine as substrate (64 mM), at 30°C and at a pH of 5.

According to the invention, the enzymatic activity is preferably determined in ulac units.

Among the heterocyclic oxidation bases which

20 can be used in the ready-to-use dye composition according to the invention, mention may be made in particular of pyrimidine derivatives and pyrazole derivatives, and the addition salts thereof with an acid.

25 Among the pyrimidine derivatives which may be mentioned more particularly are the compounds described, for example, in German patent DE 2 359 399 or Japanese patents JP 88-169 571 and JP 91-333 495,

such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, and the addition salts thereof with an acid and pyrazolo-pyrimidine derivatives such as pyrazolo[1,5-a]pyrimidine-3,7-diamine,

5 2-methylpyrazolo[1,5-a]pyrimidine-3,7-diamine,
2,5-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine,
pyrazolo[1,5-a]pyrimidine-3,5-diamine,
2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine,
3-aminopyrazolo[1,5-a]pyrimidin-7-ol, 3-amino-5-
10 methylpyrazolo[1,5-a]pyrimidin-7-ol,
3-aminopyrazolo[1,5-a]pyrimidin-5-ol, 2-(3-
aminopyrazolo[1,5-a]pyrimidin-7-ylamino)ethanol,
3-amino-7- β -hydroxyethylamino-5-methylpyrazolo-[1,5-a]pyrimidine, 2-(7-aminopyrazolo[1,5-a]pyrimidin-
15 3-ylamino)ethanol, 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)- (2-hydroxyethyl)amino]ethanol, 2-[(7-amino-
pyrazolo[1,5-a]pyrimidin-3-yl)- (2-hydroxyethyl)amino]-
ethanol, 5,6-dimethylpyrazolo[1,5-a]pyrimidine-
3,7-diamine, 2,6-dimethylpyrazolo[1,5-a]pyrimidine-
20 3,7-diamine and 2,5,N7,N7-tetramethylpyrazolo-[1,5-a]pyrimidine-3,7-diamine, and the addition salts
thereof and the tautomeric forms thereof, when a
tautomeric equilibrium exists.

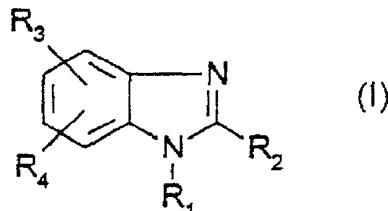
Among the pyrazole derivatives which may be
25 mentioned more particularly are the compounds described
in patents or patent applications DE 3 843 892,
DE 4 133 957, DE 4 234 886, WO 94/08969, WO 94/08970,
DE 4 234 887, FR 2 733 749, FR 2 735 685, such as

4,5-diaminopyrazole, 4,5-diamino-1-methylpyrazole,
1-benzyl-4,5-diaminopyrazole, 3,4-diaminopyrazole,
1-benzyl-4,5-diamino-3-methylpyrazole, 4-amino-1,3-
dimethyl-5-hydrazinopyrazole, 4,5-diamino-3-methyl-1-
5 phenylpyrazole, 4,5-diamino-1-tert-butyl-3-
methylpyrazole, 4,5-diamino-3-tert-butyl-1-methyl-
pyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole,
4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole,
4,5-diamino-1-ethyl-3-hydroxymethylpyrazole,
10 4,5-diamino-3-hydroxymethyl-1-methylpyrazole,
4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole and
4,5-diamino-3-methyl-1-isopropylpyrazole, and the
addition salts thereof with an acid.

Among the heterocyclic couplers which can be
15 used in the ready-to-use dye composition in accordance
with the invention, mention may be made in particular
of benzimidazole derivatives, benzomorpholine
derivatives, sesamol derivatives, pyrazoloazole
derivatives, pyrroloazole derivatives, imidazoloazole
20 derivatives, pyrazolopyrimidine derivatives,
pyrazoline-3,5-dione derivatives, pyrrolo-[3,2-d]oxazoline derivatives, pyrazolo[3,4-d]thiazole
derivatives, thiazoloazole S-oxide derivatives and
thiazoloazole S,S-dioxide derivatives, and the addition
25 salts thereof with an acid.

Among the benzimidazole derivatives which can
be used as heterocyclic couplers in the dye composition
in accordance with the invention, mention may be made

more particularly of the compounds of formula (I) below, and the addition salts thereof with an acid:



in which:

5 R₁ represents a hydrogen atom or a C₁-C₄ alkyl radical,
 R₂ represents a hydrogen atom or a C₁-C₄ alkyl or phenyl radical,
 R₃ represents a hydroxyl, amino or methoxy radical,
 R₄ represents a hydrogen atom or a hydroxyl, methoxy or
 10 C₁-C₄ alkyl radical;

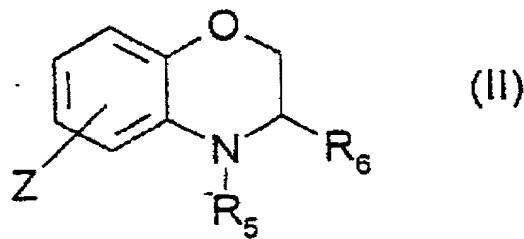
with the proviso that:

- when R₃ denotes an amino radical, then it occupies position 4,
- when R₃ occupies position 4, then R₄ occupies position
 15 7,
- when R₃ occupies position 5, then R₄ occupies position 6.

Among the benzimidazole derivatives of formula (I) above which may be mentioned more particularly are 4-hydroxybenzimidazole, 4-aminobenzimidazole, 4-hydroxy-7-methylbenzimidazole, 4-hydroxy-2-methylbenzimidazole, 1-butyl-4-hydroxybenzimidazole, 4-amino-2-methylbenzimidazole, 5,6-dihydroxybenzimidazole, 5-hydroxy-6-methoxy-

benzimidazole, 4,7-dihydroxybenzimidazole,
 4,7-dihydroxy-1-methylbenzimidazole,
 4,7-dimethoxybenzimidazole, 5,6-dihydroxy-1-methyl-
 benzimidazole, 5,6-dihydroxy-2-methylbenzimidazole and
 5 5,6-dimethoxybenzimidazole, and the addition salts
 thereof with an acid.

Among the benzomorpholine derivatives which
 can be used as heterocyclic couplers in the ready-to-
 use dye composition in accordance with the invention,
 10 mention may be made more particularly of the compounds
 of formula (II) below, and the addition salts thereof
 with an acid:

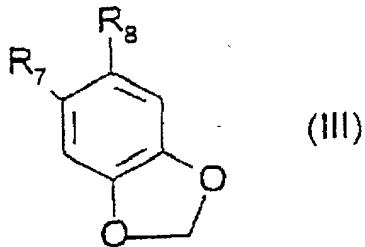


in which:

15 R₅ and R₆, which may be identical or different,
 represent a hydrogen atom or a C₁-C₄ alkyl radical,
 Z represents a hydroxyl or amino radical.

Among the benzomorpholine derivatives of
 formula (II) above which may be mentioned more
 20 particularly are 6-hydroxy-1,4-benzomorpholine,
 N-methyl-6-hydroxy-1,4-benzomorpholine and 6-amino-
 1,4-benzomorpholine, and the addition salts thereof
 with an acid.

Among the sesamol derivatives which can be used as heterocyclic couplers in the ready-to-use dye composition, mention may be made more particularly of the compounds of formula (III) below, and the addition salts thereof with an acid:



in which:

- R₇ denotes a hydroxyl, amino, (C₁-C₄)alkylamino, monohydroxy(C₁-C₄)alkylamino or polyhydroxy(C₂-C₄)alkyl-
- 10 amino radical,
- R₈ denotes a hydrogen or halogen atom or a C₁-C₄ alkoxy radical.

Among the sesamol derivatives of formula (III) above which may be mentioned more particularly 15 are 2-bromo-4,5-methylenedioxyphenol, 2-methoxy-4,5-methylenedioxyaniline and 2-(β-hydroxyethyl)amino-4,5-methylenedioxybenzene, and the addition salts thereof with an acid.

Among the pyrazoloazole derivatives which can 20 be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in the following patents and patent applications: FR 2 075 583, EP-A-119 860, EP-A-285 274,

EP-A-244 160, EP-A-578 248, GB 1 458 377, US 3 227 554,
US 3 419 391, US 3 061 432, US 4 500 630, US 3 725 067,
US 3 926 631, UA 5 457 210, JP 84/99437, JP 83/42045,
JP 84/162548, JP 84/171956, JP 85/33552, JP 85/43659,
5 JP 85/172982, JP 85/190779 as well as in the following
publications: Chem. Ber. 32, 797 (1899), Chem. Ber. 89,
2550, (1956), J. Chem. Soc. Perkin trans 1, 2047,
(1977), J. Prakt. Chem., 320, 533, (1978); the
teachings of which form an integral part of the present
10 patent application.

Pyrazoloazole derivatives which may be
mentioned most particularly are:

- 2-methylpyrazolo[1,5-b]-1,2,4-triazole,
- 2-ethylpyrazolo[1,5-b]-1,2,4-triazole,
- 15 - 2-isopropylpyrazolo[1,5-b]-1,2,4-triazole,
- 2-phenylpyrazolo[1,5-b]-1,2,4-triazole,
- 2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole,
- 7-chloro-2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole,
- 3,6-dimethylpyrazolo[3,2-c]-1,2,4-triazole,
- 20 - 6-phenyl-3-methylthiopyrazolo[3,2-c]-1,2,4-triazole,
- 6-aminopyrazolo[1,5-a]benzimidazole,

and the addition salts thereof with an acid.

Among the pyrroloazole derivatives which can
be used as heterocyclic couplers in the ready-to-use
25 dye composition in accordance with the invention,
mention may be made more particularly of the compounds
described in the following patent applications and
patents: US 5 256 526, EP-A-557 851, EP-A-578 248,

EP-A-518 238, EP-A-456 226, EP-A-488 909, EP-A-488 248,

and in the following publications:

- D.R. Liljegren Ber. 1964, 3436;
- E.J. Browne, J.C.S., 1962, 5149;
- 5 - P. Magnus, J.A.C.S., 1990, 112, 2465;
- P. Magnus, J.A.C.S., 1987, 109, 2711;
- Angew. Chem. 1960, 72, 956;
- and Rec. Trav. Chim. 1961, 80, 1075; the teachings of which form an integral part of the present patent

10 application.

Pyrroloazole derivatives which may be mentioned most particularly are:

- 5-cyano-4-ethoxycarbonyl-8-methylpyrrolo[1,2-b]-1,2,4-triazole,
- 15 - 5-cyano-8-methyl-4-phenylpyrrolo[1,2-b]-1,2,4-triazole,
- 7-amido-6-ethoxycarbonylpyrrolo[1,2-a]benzimidazole, and the addition salts thereof with an acid.

Among the imidazoloazole derivatives which 20 can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in the following patent applications and patents: US 5 441 863; JP 62-279 337; JP 06-236 011 and 25 JP 07-092 632, the teachings of which form an integral part of the present patent application.

Imidazoloazole derivatives which may be mentioned most particularly are:

- 7,8-dicyanoimidazo[3,2-a]imidazole,
- 7,8-dicyano-4-methylimidazo[3,2-a]imidazole,

and the addition salts thereof with an acid.

Among the pyrazolopyrimidine derivatives
5 which can be used as heterocyclic couplers in the
ready-to-use dye composition in accordance with the
invention, mention may be made more particularly of the
compounds described in the following patent
application: EP-A-304 001, the teaching of which forms
10 an integral part of the present patent application.

Pyrazolopyrimidine derivatives which may be
mentioned most particularly are:

- pyrazolo[1,5-a]pyrimidin-7-one,
- 2,5-dimethylpyrazolo[1,5-a]pyrimidin-7-one,
- 15 - 2-methyl-6-ethoxycarbonylpyrazolo[1,5-a]pyrimidin-7-one,
- 2-methyl-5-methoxymethylpyrazolo[1,5-a]pyrimidin-7-one,
- 2-tert-butyl-5-trifluoromethylpyrazolo[1,5-
20 a]pyrimidin-7-one,
- 2,7-dimethylpyrazolo[1,5-a]pyrimidin-5-one, and the
addition salts thereof with an acid.

Among the pyrazoline-3,5-dione derivatives
which can be used as heterocyclic couplers in the
25 ready-to-use dye composition in accordance with the
invention, mention may be made more particularly of the
compounds described in the following patent

applications and patents: JP 07-036159, JP 07-084348 and US 4 128 425, and in the following publications:

- L. WYZGOWSKA, Acta. Pol. Pharm. 1982, 39 (1-3), 83.

- E. HANNIG, Pharmazie, 1980, 35 (4), 231

5 - M.H. ELNAGDI, Bull. Chem. Soc. Jap., 46 (6), 1830, 1973

- G. CARDILLO, Gazz. Chim. Ital. 1966, 96, (8-9), 973, the teachings of which form an integral part of the present patent application.

10 Pyrazoline-3,5-dione derivatives which may be mentioned most particularly are:

- 1,2-diphenylpyrazoline-3,5-dione,

- 1,2-diethylpyrazoline-3,5-dione,

and the addition salts thereof with an acid.

15 Among the pyrrolo[3,2-d]oxazole derivatives which can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in patent application

20 JP 07 325 375, the teaching of which forms an integral part of the present patent application.

Among the pyrazolo[3,4-d]thiazole derivatives which can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in patent application JP 07 244 361 and in J. Heterocycl. Chem. 16, 13, (1979).

Among the thiazoloazole S-oxide and thiazoloazole S,S-dioxide derivatives which can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention 5 may be made more particularly of the compounds described in the following documents:

- JP 07 09 84 89;
- Khim. Geterotsilk. Soedin, 1967, p. 93;
- J. Prakt. Chem., 318, 1976, p. 12;
- 10 - Indian J. Heterocycl. Chem. 1995, 5 (2), p. 135;
- Acta. Pol. Pharm. 1995, 52 (5), 415;
- Heterocycl. Commun. 1995, 1 (4), 297;
- Arch. Pharm. (Weinheim, Ger.), 1994, 327 (12), 825.

The heterocyclic oxidation dye(s), i.e. the 15 heterocyclic oxidation base(s) and/or the heterocyclic coupler(s) preferably represent(s) from 0.0001% to 12% by weight approximately relative to the total weight of the ready-to-use dye composition, and even more preferably from 0.005% to 6% by weight approximately 20 relative to this weight.

The ready-to-use dye composition in accordance with the invention can also contain, in addition to the heterocyclic oxidation dyes defined above, at least one benzenic oxidation base and/or at 25 least one benzenic coupler and/or at least one direct dye, in particular to modify the shades or to enrich them with glints.

Among the benzenic oxidation bases which may be additionally present in the ready-to-use dye composition in accordance with the invention, mention may be made in particular of para-phenylenediamines, 5 bis(phenyl)alkylenediamines, ortho-phenylenediamines, para-aminophenols and ortho-aminophenols, and the addition salts thereof with an acid.

When they are used, these benzenic oxidation bases preferably represent from 0.0005% to 12% by weight approximately relative to the total weight of the dye composition, and even more preferably from 0.005% to 6% by weight approximately relative to this weight.

Among the benzenic couplers which may be
15 additionally present in the ready-to-use dye
composition in accordance with the invention, mention
may be made in particular of meta-phenylenediamines,
meta-aminophenols and meta-diphenols, and the addition
salts thereof with an acid.

20 When they are present, these benzenic
couplers preferably represent from 0.0001% to 10% by
weight approximately relative to the total weight of
the ready-to-use dye composition, and even more
preferably from 0.005% to 5% by weight approximately
25 relative to this weight.

In general, the addition salts with an acid which can be used in the context of the dye compositions of the invention (oxidation bases and

couples) are chosen in particular from the hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

The medium which is suitable for dyeing (or support) for the ready-to-use dye composition in accordance with the invention generally consists of water or of a mixture of water and at least one organic solvent to dissolve the compounds which would not be sufficiently water-soluble.

10 The pH of the ready-to-use composition in accordance with the invention is chosen such that the enzymatic activity of the laccase is sufficient. It is generally between 4 and 11 approximately, and preferably between 6 and 9 approximately. It can be
15 adjusted to the desired value by means of acidifying or basifying agents usually used in the dyeing of keratin fibres.

The ready-to-use dye composition in accordance with the invention can also contain various 20 adjuvants conventionally used in compositions for dyeing the hair, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures thereof, polymers, antioxidants, enzymes other than the laccases used in accordance with the invention, such 25 as, for example, peroxidases or 2-electron-oxidoreductases, penetrating agents, sequestering agents, fragrances, buffers, dispersants, film-forming

agents, preserving agents, opacifiers, thickeners and vitamins.

Needless to say, the person skilled in the art will take care to select this or these optionally 5 additional compound(s) such that the advantageous properties intrinsically associated with the ready-to-use dye composition in accordance with the invention are not, or are not substantially, adversely affected by the addition(s) envisaged.

10 The ready-to-use dye composition in accordance with the invention can be in various forms, such as in the form of liquids, creams or gels, which may be pressurized, or in any other form which is suitable for dyeing keratin fibres, and in particular 15 human hair. In this case, the heterocyclic oxidation dye(s) and optionally the additional oxidation dye(s) and the laccase-type enzyme(s) are present in the same ready-to-use composition, and consequently the said composition should be free of gaseous oxygen, so as to 20 avoid any premature oxidation of the oxidation dye(s).

A subject of the invention is also a process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, using the ready-to-use dye composition as defined above.

25 According to this process, at least one ready-to-use dye composition as defined above is applied to the fibres for a period which is sufficient to develop the desired coloration, after which the

fibres are rinsed, optionally washed with shampoo, rinsed again and dried.

The time required to develop the coloration on the keratin fibres is generally between 3 minutes 5 and 60 minutes and even more specifically between 5 minutes and 40 minutes.

According to one specific embodiment of the invention, the process includes a preliminary step consisting in separately storing, on the one hand, a 10 composition (A) comprising, in a medium which is suitable for dyeing, at least one oxidation dye chosen from the heterocyclic oxidation bases and heterocyclic couplers as defined above, and, on the other hand, a composition (B) comprising, in a medium which is 15 suitable for dyeing, at least one laccase-type enzyme, and then in mixing them together at the time of use, after which this mixture is applied to the keratin fibres.

Another subject of the invention is a multi- 20 compartment dyeing device or "kit" or any other multi-compartment packaging system, a first compartment of which contains composition (A) as defined above and a second compartment of which contains composition (B) as defined above. These devices may be equipped with a 25 means for applying the desired mixture to the hair, such as the devices described in patent FR-2 586 913 in the name of the Applicant.

The example which follows is intended to illustrate the invention without thereby limiting its scope.

DYEING EXAMPLE

5 The following ready-to-use dye compositions were prepared (contents in grams) :

COMPOSITION	1	2
2,4,5,6-Tetraaminopyrimidine sulphate (heterocyclic oxidation base)	0.65	-
para-Phenylenediamine (benzenic oxidation base)	-	0.20
Resorcinol (benzenic coupler)	0.30	-
2-Methoxy-4,5-methylenedioxyaniline monohydrochloride (heterocyclic coupler)	-	0.37
Laccase obtained from <i>Rhus vernicifera</i> at 180 units/mg, sold by the company Sigma	1.8	1.8
Common dye support (*)	(*)	(*)
Demineralized water qs	100 g	100 g

(*) : Common dye support:

- Ethanol 20.0 g
- 10 - (C8-C10)alkylpolyglucoside as an aqueous solution containing 60% active material (A.M.), sold under the name Oramix CG110® by the company Seppic 4.8 g A.M.
- 15 - Agent for pH q.s. pH = 6.5

Each of the ready-to-use dye compositions described above was applied to locks of natural grey hair containing 90% white hairs, for 40 minutes at a temperature of 30°C. The hair was then rinsed, washed 5 with a standard shampoo and then dried.

The hair was dyed in the shades given in the Table below:

EXAMPLE	Shade obtained
1	Coppery mahogany light blond
2	light blond

In the dye compositions described above, the 10 laccase from *Rhus vernicifera* at 180 units/mg, sold by the company Sigma, can be replaced with 1.0 g of laccase from *Pyricularia oryzae* at 100 units/mg, sold by the company ICN.

CLAIMS

1. Ready-to-use composition for the
oxidation dyeing of keratin fibres, and in particular
5 of human keratin fibres such as the hair, characterized
in that it comprises, in a medium which is suitable for
dyeing,

- at least one oxidation dye chosen from heterocyclic
oxidation bases and heterocyclic couplers, and
10 - at least one laccase-type enzyme,
the said composition being free of heterocyclic coupler
chosen from indole, indoline, monocyclic pyridine and
phenazine compounds and free of heterocyclic oxidation
base chosen from 4,5-diamino-6-hydroxypyrimidine and
15 3,4-diaminohydroxypyrazole.

2. Composition according to Claim 1,
characterized in that the laccase is chosen from
laccases of plant origin, of animal origin, of fungal
origin or of bacterial origin and from laccases
20 obtained by biotechnology.

3. Composition according to either of
Claims 1 and 2, characterized in that the laccase is of
plant origin and chosen from the laccases present in
extracts of Anacardiaceae plants, of Podocarpacea
25 plants, of Rosmarinus off., of Solanum tuberosum, of
Iris sp., of Coffea sp., of Daucus carota, of Vinca
minor, of Persea americana, of Catharanthus roseus, of

Musa sp., of Malus pumila, of Gingko biloba, of Monotropa hypopithys (Indian pipe), of Aesculus sp., of Acer pseudoplatanus, of Prunus persica and of Pistacia palaestina.

5 4. Composition according to Claim 1 or 2, characterized in that the laccase is of microbial origin or obtained by biotechnology.

5. Composition according to Claim 4, characterized in that the laccase is chosen from
10 laccases obtained from Polyporus versicolor, from Rhizoctonia praticola, from Rhus vernicifera, from Scytalidium, from Polyporus pinsitus, from Myceliophthora thermophila, from Rhizoctonia solani, from Pyricularia oryzae, from Trametes versicolor, from
15 Fomes fomentarius, from Chaetomium thermophile, from Neurospora crassa, from Colorius versicolor, from Botrytis cinerea, from Rigidoporus lignosus, from Phellinus noxius, from Pleurotus ostreatus, from Aspergillus nidulans, from Podospora anserina, from
20 Agaricus bisporus, from Ganoderma lucidum, from Glomerella cingulata, from Lactarius piperatus, from Russula delica, from Heterobasidion annosum, from Thelephora terrestris, from Cladosporium cladosporioides, from Cerrena unicolor, from Coriolus
25 hirsutus, from Ceriporiopsis subvermispora, from Coprinus cinereus, from Panaeolus papilionaceus, from Panaeolus sphinctrinus, from Schizophyllum commune and from Dichomitus squalens, and from variants thereof.

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6. Composition according to any one of the preceding claims, characterized in that the amount of laccase(s) is between 0.5 Lacu and 200 Lacu per 100 g of dye composition.

5 7. Composition according to any one of the preceding claims, characterized in that the heterocyclic oxidation base(s) is(are) chosen from pyrimidine derivatives and pyrazole derivatives, and the addition salts thereof with an acid.

10 8. Composition according to Claim 7, characterized in that the pyrimidine derivatives are chosen from 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine and pyrazolopyrimidine derivatives, and the addition salts thereof with an

15 acid.

9. Composition according to Claim 8, characterized in that the pyrazolopyrimidine derivatives are chosen from pyrazolo[1,5-a]pyrimidine-3,7-diamine, 2-methylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,5-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, pyrazolo[1,5-a]pyrimidine-3,5-diamine, 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine, 3-aminopyrazolo[1,5-a]pyrimidin-7-ol, 3-amino-5-methylpyrazolo[1,5-a]pyrimidin-7-ol, 3-amino-25 pyrazolo[1,5-a]pyrimidin-5-ol, 2-(3-aminopyrazolo-[1,5-a]pyrimidin-7-ylamino)ethanol, 3-amino-7- β -hydroxyethylamino-5-methylpyrazolo[1,5-a]pyrimidine, 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-ylamino)ethanol,

2- [(3-aminopyrazolo[1,5-a]pyrimidin-7-yl) - (2-hydroxyethyl)amino]ethanol, 2- [(7-aminopyrazolo[1,5-a] - pyrimidin-3-yl) - (2-hydroxyethyl)amino]ethanol, 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine,

5 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine and 2,5,N7,N7-tetramethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, and the addition salts thereof and the tautomeric forms thereof, when a tautomeric equilibrium exists.

10 10. Composition according to Claim 7, characterized in that the pyrazole derivatives are chosen from 4,5-diaminopyrazole, 4,5-diamino-1-methylpyrazole, 1-benzyl-4,5-diaminopyrazole, 3,4-diaminopyrazole, 1-benzyl-4,5-diamino-3-methylpyrazole,

15 4-amino-1,3-dimethyl-5-hydrazinopyrazole, 4,5-diamino-3-methyl-1-phenylpyrazole, 4,5-diamino-1-tert-butyl-3-methylpyrazole, 4,5-diamino-3-tert-butyl-1-methylpyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole,

20 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole, 4,5-diamino-3-hydroxymethyl-1-methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole and 4,5-diamino-3-methyl-1-isopropylpyrazole, and the addition salts thereof with an acid.

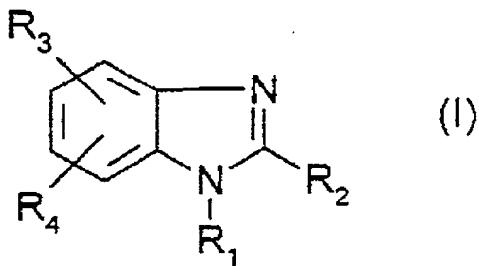
25 11. Composition according to any one of the preceding claims, characterized in that the heterocyclic coupler(s) is(are) chosen from benzimidazole derivatives, benzomorpholine derivatives,

sesamol derivatives, pyrazoloazole derivatives, pyrroloazole derivatives, imidazoloazole derivatives, pyrazolopyrimidine derivatives, pyrazoline-3,5-dione derivatives, pyrrolo[3,2-d]oxazoline derivatives,

5 pyrazolo[3,4-d]thiazole derivatives, thiazoloazole S-oxide derivatives and thiazoloazole S,S-dioxide derivatives, and the addition salts thereof with an acid.

12. Composition according to Claim 11,

10 characterized in that the benzimidazole derivatives are chosen from the compounds of formula (I) below, and the addition salts thereof with an acid:



in which:

15 R_1 represents a hydrogen atom or a C_1-C_4 alkyl radical,
 R_2 represents a hydrogen atom or a C_1-C_4 alkyl or phenyl radical,
 R_3 represents a hydroxyl, amino or methoxy radical,
 R_4 represents a hydrogen atom or a hydroxyl, methoxy or

20 C_1-C_4 alkyl radical;

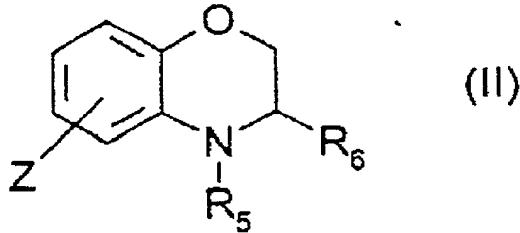
with the proviso that:

- when R_3 denotes an amino radical, then it occupies position 4,

- when R_3 occupies position 4, then R_4 occupies position 7,
- when R_3 occupies position 5, then R_4 occupies position 6.

5 13. Composition according to Claim 12,
 characterized in that the benzimidazole derivatives are
 chosen from 4-hydroxybenzimidazole, 4-amino-
 benzimidazole, 4-hydroxy-7-methylbenzimidazole,
 4-hydroxy-2-methylbenzimidazole, 1-butyl-4-hydroxy-
 10 benzimidazole, 4-amino-2-methylbenzimidazole,
 5,6-dihydroxybenzimidazole, 5-hydroxy-6-methoxy-
 benzimidazole, 4,7-dihydroxybenzimidazole,
 4,7-dihydroxy-1-methylbenzimidazole, 4,7-dimethoxy-
 benzimidazole, 5,6-dihydroxy-1-methylbenzimidazole,
 15 5,6-dihydroxy-2-methylbenzimidazole and 5,6-dimethoxy-
 benzimidazole, and the addition salts thereof with an
 acid.

14. Composition according to Claim 11,
 characterized in that the benzomorpholine derivatives
 20 are chosen from the compounds of formula (II) below,
 and the addition salts thereof with an acid:

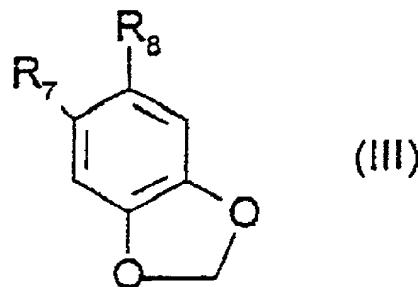


in which:

R_5 and R_6 , which may be identical or different, represent a hydrogen atom or a C_1 - C_4 alkyl radical, Z represents a hydroxyl or amino radical.

15. Composition according to Claim 14,
 5 characterized in that the benzomorpholine derivatives are chosen from 6-hydroxy-1,4-benzomorpholine, N-methyl-6-hydroxy-1,4-benzomorpholine and 6-amino-1,4-benzomorpholine, and the addition salts thereof with an acid.

10 16. Composition according to Claim 11,
 characterized in that the sesamol derivatives are chosen from the compounds of formula (III) below, and the addition salts thereof with an acid:



15 in which:
 - R_7 denotes a hydroxyl, amino, $(C_1$ - C_4)alkylamino, monohydroxy(C_1 - C_4)alkylamino or polyhydroxy(C_2 - C_4)alkylamino radical,
 - R_8 denotes a hydrogen or halogen atom or a C_1 - C_4 alkoxy radical.

20 17. Composition according to Claim 16,
 characterized in that the sesamol derivatives are chosen from 2-bromo-4,5-methylenedioxyphenol,

2-methoxy-4,5-methylenedioxyaniline and 2-(β -hydroxy-ethyl)amino-4,5-methylenedioxobenzene, and the addition salts thereof with an acid.

18. Composition according to Claim 11,
5 characterized in that the pyrazoloazole derivatives are chosen from:

- 2-methylpyrazolo[1,5-b]-1,2,4-triazole,
- 2-ethylpyrazolo[1,5-b]-1,2,4-triazole,
- 2-isopropylpyrazolo[1,5-b]-1,2,4-triazole,
- 10 - 2-phenylpyrazolo[1,5-b]-1,2,4-triazole,
- 2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole,
- 7-chloro-2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole,
- 3,6-dimethylpyrazolo[3,2-c]-1,2,4-triazole,
- 6-phenyl-3-methylthiopyrazolo[3,2-c]-1,2,4-triazole,
- 15 - 6-aminopyrazolo[1,5-a]benzimidazole,

and the addition salts thereof with an acid.

19. Composition according to Claim 11,
characterized in that the pyrroloazole derivatives are chosen from:

- 20 - 5-cyano-4-ethoxycarbonyl-8-methylpyrrolo[1,2-b]-1,2,4-triazole,
- 5-cyano-8-methyl-4-phenylpyrrolo[1,2-b]-1,2,4-triazole,
- 7-amido-6-ethoxycarbonylpyrrolo[1,2-a]benzimidazole,

25 and the addition salts thereof with an acid.

20. Composition according to Claim 11,
characterized in that the imidazoloazole derivatives are chosen from:

- 7,8-dicyanoimidazo[3,2-a]imidazole,
- 7,8-dicyano-4-methylimidazo[3,2-a]imidazole,
and the addition salts thereof with an acid.

21. Composition according to Claim 11,
5 characterized in that the pyrazolopyrimidine
derivatives are chosen from:
- pyrazolo[1,5-a]pyrimidin-7-one,
- 2,5-dimethylpyrazolo[1,5-a]pyrimidin-7-one,
- 2-methyl-6-ethoxycarbonylpyrazolo[1,5-a]pyrimidin-
10 7-one,
- 2-methyl-5-methoxymethylpyrazolo[1,5-a]pyrimidin-
7-one,
- 2-tert-butyl-5-trifluoromethylpyrazolo[1,5-
a]pyrimidin-7-one,
15 - 2,7-dimethylpyrazolo[1,5-a]pyrimidin-5-one, and the
addition salts thereof with an acid.

22. Composition according to Claim 11,
characterized in that the pyrazoline-3,5-dione
derivatives are chosen from:

20 - 1,2-diphenylpyrazoline-3,5-dione,
- 1,2-diethylpyrazoline-3,5-dione,
and the addition salts thereof with an acid.

23. Composition according to any one of the
preceding claims, characterized in that the
25 heterocyclic oxidation dye(s) represent(s) from 0.0001%
to 12% by weight relative to the total weight of the
ready-to-use dye composition.

24. Composition according to Claim 23, characterized in that the heterocyclic oxidation dye(s) represent(s) from 0.005% to 6% by weight relative to the total weight of the ready-to-use dye composition.

5 25. Composition according to any one of the preceding claims, characterized in that it contains at least one benzenic oxidation base chosen from para-phenylenediamines, bis(phenylalkylenediamines, orthophenylenediamines, para-aminophenols and ortho-10 aminophenols, and the addition salts thereof with an acid, and/or at least one benzenic coupler chosen from meta-phenylenediamines, meta-aminophenols and meta-diphenols and the addition salts thereof with an acid, and/or at least one direct dye.

15 26. Composition according to any one of the preceding claims, characterized in that the addition salts with an acid are chosen from the hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

20 27. Composition according to any one of the preceding claims, characterized in that the medium which is suitable for dyeing consists of water or of a mixture of water and at least one organic solvent.

28. Composition according to any one of the 25 preceding claims, characterized in that it has a pH of between 4 and 11.

29. Process for dyeing keratin fibres, and in particular human keratin fibres such as the hair,

characterized in that at least one ready-to-use dye composition as defined in any one of the preceding claims is applied to the said fibres, for a period which is sufficient to develop the desired coloration.

5 30. Process according to Claim 29, characterized in that it includes a preliminary step which consists in separately storing, on the one hand, a composition (A) comprising, in a medium which is suitable for dyeing, at least one heterocyclic 10 oxidation dye as defined in any one of Claims 1, 7 to 24 and 26, and, on the other hand, a composition (B) comprising in a medium which is suitable for dyeing, at least one laccase-type enzyme, and then in mixing them together at the time of use, after which this mixture 15 is applied to the keratin fibres.

31. Multi-compartment dyeing device or "kit", characterized in that it includes a first compartment comprising composition (A) as defined in Claim 30 and a second compartment comprising 20 composition (B) as defined in Claim 30.

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Declaration and Power of Attorney for Patent Application

Déclaration et Pouvoir pour Demand de Brevet

French Language Declaration

En tant que l'inventeur nommé ci-après, je déclare par le présent acte que:

Mon domicile, mon adresse postale et ma nationalité sont ceux figurant ci-dessous à côté de mon nom.

Je crois être le premier inventeur original et unique (si un seul nom est mentionné ci-dessous), ou l'un des premiers co-inventeurs originaux (si plusieurs noms sont mentionnés ci-dessous) de l'objet revendiqué, pour lequel une demande de brevet a été déposée concernant l'invention intitulée

et dont la description est fournie ci-joint à moins que la case suivante n'ait été cochée:

a été déposée le _____
sous le numéro de demande des Etats-Unis ou le
numéro de demande international PCT
_____ et modifiée
_____ (les cas échéant).

Je déclare par le présent acte avoir passé en revue et compris le contenu de la description ci-dessus, revendications comprises, telles que modifiées par toute modification dont il aura été fait référence ci-dessus.

Je reconnaiss devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations.

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

**KERATINOUS FIBRE OXIDATION DYEING
COMPOSITION CONTAINING A LACCASE AND
DYEING METHOD USING SAME**

the specification of which is attached hereto unless the following box is checked:

was filed on December 22, 1998 as United States Application Number or PCT International Application Number PCT/FR98/02831 and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

French Language Declaration

Je revendique par le présent acte avoir la priorité étrangère, en vertu du Titre 35, § 119(a)-(d) ou § 365(b) du Code des Etats-Unis, sur toute demande étrangère de brevet ou certificat d'inventeur ou, en vertu du Titre 35, § 365(a) du même Code, sur toute demande internationale PCT désignant au moins un pays autre que les Etats-Unis et figurant ci-dessous et, en cochant la case, j'ai aussi indiqué ci-dessous toute demande étrangère de brevet, tout certificat d'inventeur ou toute demande internationale PCT ayant une date de dépôt précédant celle de la demande à propos de laquelle une priorité est revendiquée.

Prior foreign application(s)
Demande(s) de brevet antérieure(s)

98/00,258 (Number) (Numéro)	France (Country) (Pays)
(Number) (Numéro)	(Country) (Pays)

Je revendique par le présent acte tout bénéfice, en vertu du Titre 35, § 119(e) du Code des Etats-Unis, de toute demande de brevet provisoire effectuée aux Etats-Unis et figurant ci-dessous.

(Application No.) (N° de demande)	(Filing Date) (Date de dépôt)
(Application No.) (N° de demande)	(Filing Date) (Date de dépôt)

Je revendique par le présent acte tout bénéfice, en vertu du Titre 35, § 120 du Code des Etats-Unis, de toute demande de brevet effectuée aux Etats-Unis, ou en vertu du Titre 35, § 365(c) du même Code, de toute demande internationale PCT désignant les Etats-Unis et figurant ci-dessous et, dans la mesure où l'objet de chacune des revendications de cette demande de brevet n'est pas divulgué dans la demande antérieure américaine ou internationale PCT, en vertu des dispositions du premier paragraphe du Titre 35, § 112 du Code des Etats-Unis, je reconnais devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations, dont laquelle est devenue disponible entre la date de dépôt de la demande antérieure, et la date de dépôt de la demande nationale ou internationale PCT de la présente demande:

(Application No.) (N° de demande)	(Filing Date) (Date de dépôt)
(Application No.) (N° de demande)	(Filing Date) (Date de dépôt)

I hereby claim foreign priority under Title 35, United States Code, § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International Application which designated at least one country other than the United States, listed below, and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Priority Not Claimed
Droit de priorité non revendiqué

13 January 1998
(Day/Month/Year Filed)
(Jour/Mois/Anné de dépôt)

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT International Application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International Application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose any or all information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

(Status) (patented, pending, abandoned)
(Status) (breveté, en cours d'examen, abandonné)

Je déclare par le présent acte que toute déclaration ci-incluse est, à ma connaissance, vérifique et que toute déclaration formulée à partir de renseignements ou de suppositions est tenue pour vérifique; et de plus, que toutes ces déclarations ont été formulées en sachant que toute fausse déclaration volontaire ou son équivalent est passible d'une amende ou d'une incarcération, ou des deux, en vertu de la Section 1001 du Titre 18 du Code des Etats-Unis, et que de telles déclarations volontairement fausses risquent de compromettre la validité de la demande de brevet ou du brevet délivré à partir de celle-ci.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

French Language Declaration

POUVOIRS: En tant que l'inventeur cité, je désigne par la présente l'(les) avocat(s) et/ou agent(s) suivant(s) pour qu'ils poursuive(nt) la procédure de cette demande de brevet et traite(nt) toute affaire s'y rapportant avec L'Office des brevets et des marques: *(mentionner le nom et le numéro d'enregistrement)*.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this patent application and transact all business in the Patent and Trademark Office connected therewith: *(list name and registration number):*

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER, L.L.P., Reg. No. 22,540; Douglas B. Henderson, Reg. No. 20,291; Ford F. Farabow, Jr., Reg. No. 20,630; Arthur S. Garrett, Reg. No. 20,338; Donald R. Dunner, Reg. No. 19,073; Brian G. Brunsbold, Reg. No. 22,593; Tipton D. Jennings, IV, Reg. No. 20,645; Jerry D. Voight, Reg. No. 23,020; Laurence R. Heftel, Reg. No. 20,827; Kenneth E. Payne, Reg. No. 23,098; Herbert H. Mintz, Reg. No. 26,691; C. Larry O'Rourke, Reg. No. 26,014; Albert J. Santorelli, Reg. No. 22,610; Michael C. Elmer, Reg. No. 25,857; Richard H. Smith, Reg. No. 20,609; Stephen L. Peterson, Reg. No. 26,325; John M. Romary, Reg. No. 26,331; Bruce C. Zoller, Reg. No. 27,680; Dennis P. O'Reilley, Reg. No. 27,932; Allen M. Sokal, Reg. No. 26,695; Robert D. Bajefsky, Reg. No. 25,387; Richard L. Stroup, Reg. No. 28,478; David W. Hill, Reg. No. 28,220; Thomas L. Irving, Reg. No. 28,619; Charles E. Lipsey, Reg. No. 28,165; Thomas W. Winland, Reg. No. 27,605; Basil J. Lewis, Reg. No. 28,818; Martin I. Fuchs, Reg. No. 28,508; E. Robert Yoches, Reg. No. 30,120; Barry W. Graham, Reg. No. 29,924; Susan Haberman Griffen, Reg. No. 30,907; Richard B. Racine, Reg. No. 30,415; Thomas H. Jenkins, Reg. No. 30,857; Robert E. Converse, Jr., Reg. No. 27,432; Clair X. Mullen, Jr., Reg. No. 20,348; Christopher P. Foley, Reg. No. 31,354; John C. Paul, Reg. No. 30,413; Roger D. Taylor, Reg. No. 28,992; David M. Kelly, Reg. No. 30,953; Kenneth J. Meyers, Reg. No. 25,146; Carol P. Einaudi, Reg. No. 32,220; Walter Y. Boyd, Jr., Reg. No. 31,738; Steven M. Anzalone, Reg. No. 32,095; Jean B. Fordis, Reg. No. 32,984; Barbara C. McCurdy, Reg. No. 32,120; James K. Hammond, Reg. No. 31,964; Richard V. Burgujian, Reg. No. 31,744; J. Michael Jakes, Reg. No. 32,824; Dirk D. Thomas, Reg. No. 32,600; Thomas W. Banks, Reg. No. 32,719; Christopher P. Isaac, Reg. No. 32,616; Bryan C. Diner, Reg. No. 32,409; M. Paul Barker, Reg. No. 32,013; Andrew Chanko Sonu, Reg. No. 33,457; David S. Forman, Reg. No. 33,694; Vincent P. Kovalick, Reg. No. 32,867; James W. Edmondson, Reg. No. 33,871; Michael R. McGurk, Reg. No. 32,045; Joann M. Neth, Reg. No. 36,363; Gerson S. Panitch, Reg. No. 33,751; Cheri M. Taylor, Reg. No. 33,216; Charles E. Van Horn, Reg. No. 40,266; Linda A. Wadler, Reg. No. 33,218; Jeffrey A. Berkowitz, Reg. No. 36,743; Michael R. Kelly, Reg. No. 33,921; and James B. Monroe, Reg. No. 33,971; and Thalia V. Warnement, Reg. No. 39,064; Michele C. Bosch, Reg. No. 40,524; Allen R. Jensen, Reg. No. 28,224; Mark D. Sweet, Reg. No. 41,469; and Anthony M. Gutowski, Reg. No. 38,742.

Addresser toute correspondance à:

Send all Correspondence to:

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER, L.L.P.
1300 I Street, N.W., Washington, D.C. 20005,
Telephone No. (202) 408-4000.

Addresser tout appel téléphonique à:
*(nom et numéro de téléphone)*Direct all Telephone Calls to:
(name and telephone number)

Thomas L. Irving, Reg. No. 28,619
Telephone Number (202) 408-4082

Nom complet de l'unique ou premier inventeur: <i>Gérard LANG</i>			Full name of sole or first inventor Gérard LANG
Signature de l'inventeur	Date	Inventor's signature <i>Gérard Lang</i> 08/21/2008	
Domicile	Residence 51B, rue Robert Thomas, F-95390 Saint Prix, France <i>FR</i>		
Nationalité:	Citizenship French		
Adresse postale:	Post Office Address Same as residence		
Nom complet du second co-inventeur, le cas échéant: <i>Jean COTTERET</i>			Full name of second joint inventor, if any: Jean COTTERET
Signature du second inventeur	Date	Second Inventor's signature <i>Jean COTTERET</i>	Date 08/21/2008
Domicile:	Residence 13, rue du Pré Roussel, F-78480 Verneuil sur Seine, France		
Nationalité:	Citizenship French <i>FR</i>		
Adresse postale:	Post Office Address Same as residence		
Nom complet du third co-inventeur, le cas échéant:			Full name of third joint inventor, if any:
Signature d'inventeur	Date	Third Inventor's signature	Date
Domicile	Residence		
Nationalité:	Citizenship		
Adresse postale:	Post Office Address		